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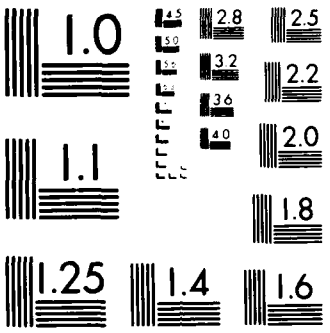

REPORT SD-TR-86-36

Microbeam Quantitative Analysis of Mixed Oxides in a Tungsten Matrix

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20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

The technique of energy dispersed x-ray spectrometry (EDXS) for quantitative analysis is compared against the standard technique of wavelength dispersed x-ray spectrometry (WDXS). The sample configuration under consideration is that of mixed oxides of calcium-barium-aluminum embedded in a tungsten matrix. We have found that the results of the oxide composition obtained by the two techniques agree to better than 5%.

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This report has been reviewed by the Public Affairs Office (PAS) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nationals.

This technical report has been reviewed and is approved for publication. Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

Doug R Case

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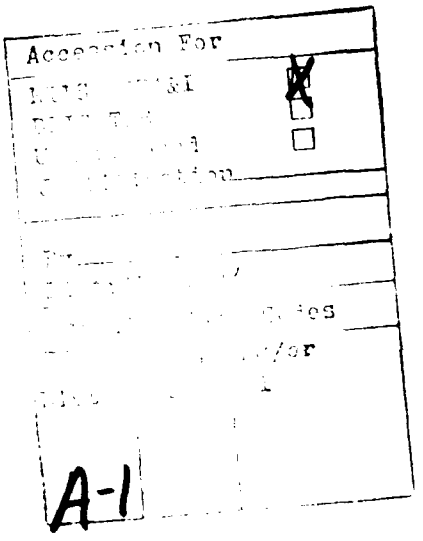

FIGURES

TABLE

I. INTRODUCTION

Our work was motivated by an interest in thermionic emitters used in microwave transmitter tubes (traveling-wave tubes) for space communication. These emitters are the so-called impregnated cathodes that consist of porous tungsten structures of about 80% bulk density so that the pores form a connected network. The pores are impregnated with mixed oxides of barium, calcium, and aluminum from melt. In operation, the tungsten matrix reacts with the mixed oxide impregnants to produce a continuous supply of barium to the emitting surface, ensuring a low work-function surface during the life of the satellite. The ability to make quantitative analyses of the embedded oxides or impregnants allows us to examine composition uniformity and identify the products of chemical reaction which accompany cathode operation.

Energy dispersed x-ray spectrometry (EDXS) is a convenient technique, but its ability to do quantitative analysis on samples having a complex geometry such as those containing embedded materials is often questioned. The findings described below, however, indicate that with pore sizes of the order of a few micrometers and with suitable sample preparation, it is possible to obtain good quantitative agreements between EDXS and the standard technique of wavelength dispersed x-ray spectrometry (WDXS).

II. EXPERIMENTAL PROCEDURE

Each sample was sectioned so as to expose its interior, and was polished flat in order to establish a well-defined geometric relationship between the surface of the specimen and the analyzer system; this is an important procedure for obtaining quantitative results. The mixed oxide impregnant material is loosely held in the tungsten matrix, however, and must be rigidly supported during sectioning and polishing. A technique was developed to support the oxide material in place by infiltrating the entire structure with plastic so that the impregnants would not be smeared during polishing. The details of sample preparation are described elsewhere.[1]

A micrograph of a polished surface is shown in Fig. 1. The light area is tungsten and the dark regions are pores, which now contain impregnant materials supported by plastic. The features inside the pores represent different phases of oxides and will be described below in greater detail. Beam analysis is made directly on the supported materials, pore by pore. To avoid interference from the tungsten matrix, the analyzing beams were directed to the interior of the pores. The experimental conditions are described in Table 1 for both wavelength and energy dispersed analyses.

In addition to these techniques, it turned out that different oxide phases could also be distinguished by their grey scale as seen in ordinary secondary-electron SEM photographs. A "calibration," or the actual identification of regions having a particular grey level with a given oxide phase, of course, requires actual quantitative analysis by WDXS. In Fig. 1 the oxide phases that were so identified are indicated. The grey-scale delineation was extremely helpful in directing the beam to perform analysis of the individual phases.

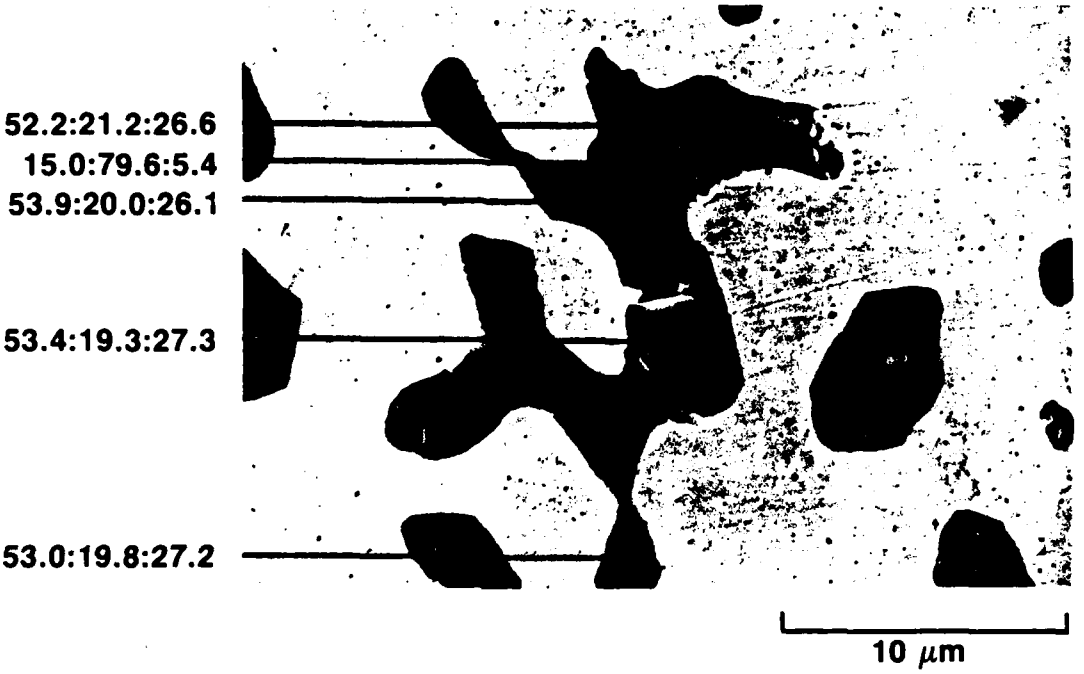

Fig. 1. Micrograph of Polished Cross Section of Impregnated Cathode. Values are BaO:CaO:Al_2O_3 mole ratios.

Table 1. Experimental Conditions for Wavelength and Energy Dispersal Analysis

	WDXS	EDXS
Instrument	Cameca Camebax-Micro	Cambridge S 200; Tracor Northern 5500
Electron energy	15 keV	15 keV
Sample current	9 nA	0.05-0.1 nA
Take-off angle	40°	35°
Counting time	20 s peak, 10 s background	150 s
Analyzed element, line, standard	Ba, L, $BaSO_4$	Ba, L, $BaSO_4$
	Al, K, Al_2O_3	Al, K, Al_2O_3
	Ca, K, $CaSiO_3$	Ca, K, $CaSiO_3$
	W, M, W	W, M, W

III. RESULTS

The results of measuring the oxide composition in 30 pores in one sample are shown Fig. 2 in a phase diagram[2] for the system of BaO, CaO, and Al_2O_3. Each point on the phase diagram represents the result obtained on one pore, and the average values of 30 pores are also indicated. Figure 2 (bottom) shows the data obtained by EDXS, while Fig. 2 (top) displays the same results on the same sample in approximately the same region but obtained by electron microprobe. The scatter in the phase diagram in each case is attributed mostly to the nonuniformity of the sample itself. The agreement between the EDXS and the microprobe results is good; the methods agree to about 5%.

After a cathode is operated at elevated temperatures, the reaction of the oxide impregnants with the tungsten matrix results in the formation of different oxide phases; the details depend on the operating conditions and on the positior of the phases in the sample, because there is a continuously decreasing barium vapor pressure towards the emitting surface. The particular region in Fig. 1 shows the existence of several phases: dibarium calcium tungstate near the tungsten wall; calcium oxide (which has separated into sizable particles); and the remaining barium, calcium, and aluminum mixed oxides. When the beam was directed to these different regions, the results shown in Fig. 3 were obtained. The points scattered on the line joining the end points of barium aluminate and calcium oxide correspond to regions in the sample which contained a mixture of these two phases. Below that line are points corresponding to a composition close to that of the starting material (Fig. 2). The points at the lower portion of the phase diagrams have a ratio of barium oxide to calcium oxide of 2:1, and in each case a tungsten signal showing a material composition of dibarium calcium tungstate was observed. The similarity of the two sets of data shows that the two techniques gave very comparable results.

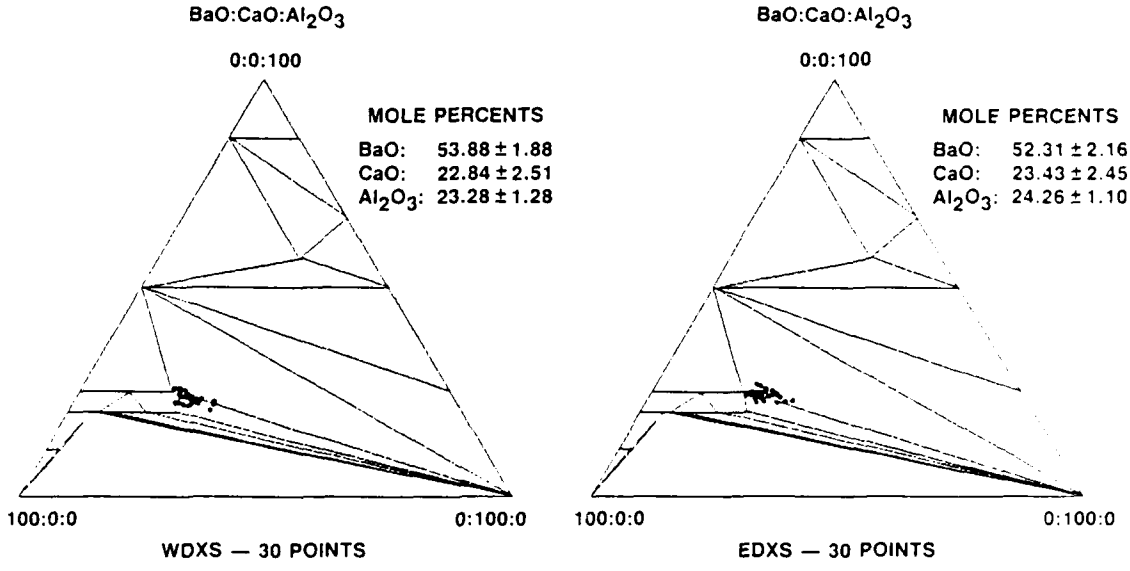

Fig. 2. Analysis of Unused Cathode

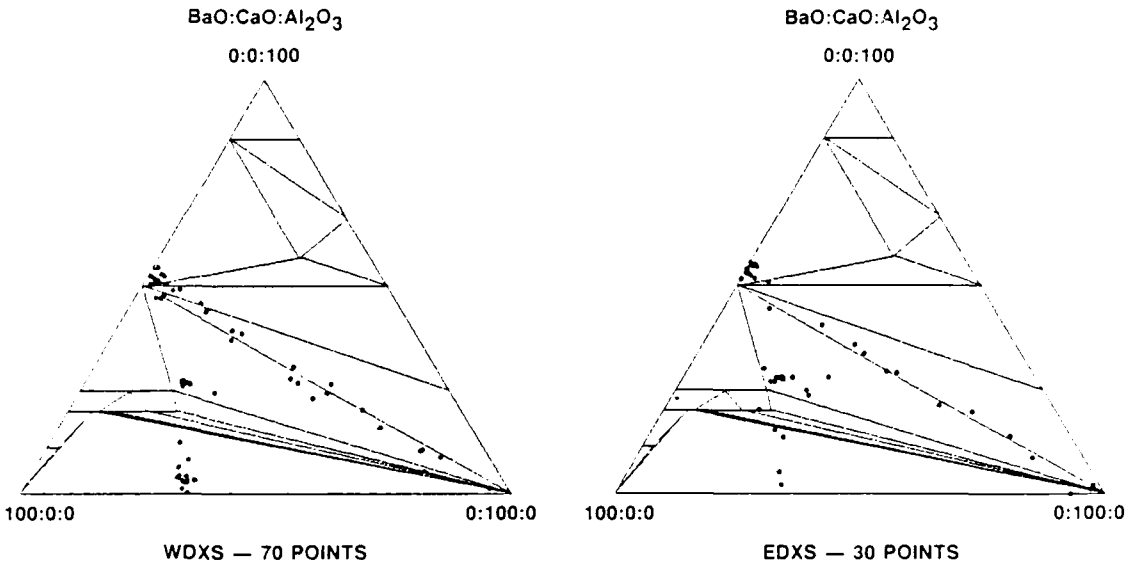

Fig. 3. Analysis of Used Cathode

IV. CONCLUSION

The technique of EDXS can be used to obtain quantitative analysis results of oxides in a metal matrix which are in good agreement with results obtained by WDXS. Sample preparation that supports the embedded material and provides a well-defined geometry in the analysis chamber is essential to obtaining the favorable comparison. The analysis volumes were large enough in this case so as not to give significant signals from the matrix. In general the matrix can still absorb some of the x-rays and so affect the accuracy of the analysis, but the extent will depend on analysis geometry. In our case, the two techniques employed different take-off angles; the good agreement of the results suggests that the matrix absorption effect here is not large.

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